Collective vibrations and soft modes in hard sphere colloids
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2 Experimental Techniques
2.1 What are Colloids?

The term “colloid” comes from the Greek word “Kolla” (means glue) was first coined by Thomas Graham in 1861 to distinguish those materials in aqueous solution that would not pass through a parchment membrane from those that would. The term emphasizes their low rate of diffusion and lack of crystallinity. Graham deduced that the low rate of diffusion implied that the particles were fairly large - at least 1 nm in diameter in modern terms. Thus colloids are homogeneous mixtures differing from molecular solutions and suspensions by the size of the particles. Particles in a solution are about the size of molecules, approximately 1 nanometer.

![Solution, Colloidal solution, Suspension](image)

**Figure 2.1:** Depending on the size of solvent particles dispersions are classified into solutions ($\sigma < 1 \text{nm}$), colloidal suspensions ($\sim 100 \text{nm}$) and granular paste, $\sigma > 1 \mu \text{m}$.

or below in diameter. Those that form granular paste are larger than 1 $\mu \text{m}$ and finally, colloidal particles range in size roughly from $\approx 1 \text{nm}$ to 1 micron. Note that these size limits are not rigid, for in some special cases emulsions or slurries, particles of larger size is present, also, system containing fibres only two dimensions are in the colloid range.

Every colloidal suspension consists of two separate phases: a dispersed phase where one substance is dispersed uniformly in a finely divided state throughout a dispersion medium or continuous phase. Both the phases could be either solid, liquid or gas. Some familiar examples of colloids are, fogs, mists, smokes where fine liquid droplets dispersed in a gas - aerosols, milk - dispersions of fat in an aqueous phase, paint, mud, slurries, where solid particles dispersed in a liquid medium - sols.
2.2 Colloids as a Model System

Besides a large numbers of industrial and daily life use - colloids have been successfully used to study the properties and processes of atomic systems and phenomena like glasses, nucleation etc. as elaborated below.

2.2 Colloids as a Model System

The static and dynamic properties of colloidal suspensions share many features of simple atomic liquids. In particular, the colloidal particles forms fluids, crystals and undergo a glass transition [1]-[3] at higher volume fraction similar to atomic systems. The much smaller length scales of atoms/ molecules compared to colloids results in faster dynamics - thereby giving rise to very small relaxation times which often limits the experimental accessibility of the physical process in these systems. Now, the relaxation of density fluctuations in a colloidal system is much slower, the usual Brownian time $\tau_B = \frac{\eta d^3}{k_B T} \approx 1s^{-1}$, the particle take to diffuse over its own radius is of the order of $\sim 1s^{-1}$ allowing for detailed experimental studies. The other important aspect is that generally the interactions between the colloidal particles can be described by an ef-
fective pairwise potential as in simple atomic fluids. These potentials determine the microstructure and the macroscopic thermodynamic properties through the use of classical statistical mechanics. This establishes a direct analogy between the two systems. Furthermore, the interaction potentials in colloidal systems are tunable [4] in several ways giving easier access to transitions between a variety of phases. Colloidal particles thus can be considered as ‘macro-atoms’ with interparticle distances comparable to the visible light wavelength and slow relaxation, which provides a reasonable model system of atomic or molecular systems at different time and length scales.

![Image](image_url)

Figure 2.3: One of the earliest study of real space imaging of colloidal crystal as observed by van-Blaaderen and Wiltzius in 1995 [6].

In the past decades, a number of techniques such as static and dynamic light scattering, small angle X-ray and neutron scattering, video microscopy have been extensively used to probe colloidal systems. The findings by [1], using light scattering, showed that monodisperse colloids replicates some of the phase behavior of the of atomic systems. The use of laser scanning confocal microscopy in colloidal systems is a relatively recent development. While scattering studies gives access to the bulk behavior, confocal microscopy enables direct visualization and recording of the particle motions providing information about the microscopic details of these systems. One of first studies is by Yoshida et al [5] in 1991 who looked deep inside a sample of polystyrene latex colloids and observed hexagonal ordering of the spheres. van Blaaderen and Wiltzius [6] extended the capability of confocal microscopy to denser systems, imaging
spheres with packing fractions of 60% to observe the structure in the colloidal glass and crystalline phases. A two dimensional image of the colloidal crystal as obtained by them is shown in Fig. 2.3. It has by now become one of the most powerful and growingly popular tools in colloid science. In the present thesis we use laser scanning confocal microscopy to visualize fluorescent colloidal particles discussed in detail in sec 2.5.1.

2.3 Hard Sphere Systems

One of the simplest system that can be mimicked by colloidal suspensions is the hard sphere system. The hard sphere system is defined as a set of impenetrable spheres where the interaction becomes infinitely repulsive as two adjacent spheres overlaps, otherwise it is zero. Interparticle interactions in an simple atomic or molecular fluid are well described by short range highly repulsive branch along with a longer range weak attraction. In 1954, in a landmark theory, Robert Zwanzig [7], first introduced the perturbation theory of liquid state where Lennard-Jones potential is treated as a perturbation over a reference state made of hard spheres. This theory is particularly successful describing the high temperature behavior of atomic fluid. The results were re-affirmed by the first-order perturbation expansion of Weeks, Chandler and Andersen [8, 9]. All this

![Figure 2.4: Pictorial representation of different phases, stable fluid and crystalline phase as well as metastable glassy phase in hard sphere systems.](image_url)
work has drawn much attention to physics of hard sphere systems and it has gained much importance as a simplified reference state for liquids.

Phase Behavior

The other interests in hard spheres comes from the fact that it is the simplest system to show a fluid-solid transition [10, 11, 12] as well as a glass transition at higher concentration. The free energy of the hard sphere systems constitutes only of the entropy, as there is no potential energy contribution due to the zero interaction between the spheres unless they overlap. Thus while in other system there is competition between energy and entropy, the transitions in hard spheres are purely “entropy driven”. For example, the freezing of hard spheres is caused by a competition between two contributions to the entropy $S$, associated respectively with the spatial configuration of the particles and the free volume available for local motions of the particles. Freezing occurs at a concentration at which the entropy lost by the system on developing long-ranged spatial order is more than offset by the entropy gained from the larger free volumes available to the particles.

![Figure 2.5: Schematic phase diagram of hard sphere system.](image)

Thus the HS phase behavior depends only on a single parameter, its
volume fraction $\phi$. For $N$ hard spheres of radius $\sigma$ and volume $V$ the volume fraction is $\phi = 4/3\pi \sigma^3 (N/V)$. Below the freezing transition \cite{12} $\phi_f = 0.494$, the equilibrium state is a fluid, an disorderly arrangement of particles where the system is able to visit all accessible micro-states in phase space (ergodic). Beyond $\phi = 0.545$ the thermodynamically stable state is crystalline up to the close packing fraction 0.74. Fluid and solid co-exists in between the range $0.494 < \phi < 0.545$. Existence of another metastable disordered branch has been observed that starts at $\phi = 0.494$ up to the random close packing 0.64. A number of simulations and experiments on hard spheres system in past decades recognizes these higher density metastable states as glassy states. The diagram in Fig. 2.5 depicts the hard sphere phase behavior.

The glass transition in hard sphere system has been an issue of debate. The first theoretical calculations that put this phenomenon on firm footing is the mode coupling calculation by Gotze et. al \cite{13, 14}, in the 1980s, which predicts glass transition at a volume fraction $\phi \approx 0.52$. Starting with a lower density disordered state and carefully “compressing” it to avoid crystallization leads eventually to such metastable states. This is now a widely used way to prepare such glassy states in computer simulations.

![Figure 2.6: Experimental observation of equilibrium and non-equilibrium phases in dense PMMA suspensions as studied by Pusey and Megen \cite{1}]

On experimental front, the pioneering work of Pusey and Megen (Fig. 2.6) has shown that the suspensions of sterically stabilized PMMA particles (polymethyl methacrylate) at various concentration well replicates the phase behavior of the hard spheres. In addition, they found that the
samples above $\phi \approx 0.58$ that should crystallize, remained amorphous for months. Following this observation, a number of dynamic light scattering (DLS) experiments have been done which show that this failure to crystallize is indeed particles being trapped into a glassy state [15, 16, 17]. The intermediate scattering function $f(q, t)$ that is measured in these DLS experiments shown that it did not completely decay to zero above a volume fraction $\phi \approx 0.58$, indicating the onset of nonergodicity and thus a glass transition in hard spheres. Later, a detailed study by them along with their initial DLS results showed that MCT predicts $f(q, t)$ accurately, provided the theoretical $\phi$ is scaled by $0.58/0.52 = 1.12$ [18].

### 2.4 Sample Preparation

![Diagram of steric stabilization of PMMA particles](image)

Figure 2.7: Schematic diagram of steric stabilization of PMMA particles where a layer of polymer is grafted on the outer surface. The repulsive force between two particles originates from the interaction of such polymer layers as they approach close to each other.

In the present experiments we have used sterically stabilized PMMA (poly methylmethacrylate) particles to prepare hard sphere systems, which is obtained by the bulk polymerization of MMA (methyl methacrylate) monomers. The PMMA particles we use here is synthesized by Andrew Schofield [19]. They are transparent and colorless thermoplastic that is hard and stiff. The dielectric nature of the PMMA particles in a solvent gives rise to long range attractive van der Waals between the spheres. So, when two particles come closer they tend to stick to each other leading
to irreversible aggregation. Here, by matching the refractive index of the solvent with that of the particles, the van der Waals forces are made very small. In addition a stabilizing mechanism is used to create a positive potential barrier between the particles so as to avoid flocculation. One of the ways to achieve this is steric stabilization [20, 21] of the particles where a ‘protective’ layer of polymer / macro molecules are grafted on the surface of the PMMA spheres. Interactions between these layers of two adjacent particles results strong enough repulsion between the surfaces sufficient to suppress the van der Waals attraction.

The present set of particles with a radius of about 650nm are sterically stabilized by a layer of poly-12-hydroxystearic acid (PHSA). The thickness of the layer is 10 – 20nm - a very small fraction of the radius. The repulsive potential arising due to the interpenetration of polymer layers are relatively steep giving rise to ‘hard sphere’ like interaction.

To prepare the dispersion, these PMMA particles are suspended in a mixture of Cis-decaaline and Cyclo Heptyle Bromide (CHB) with a volume ratio of 1 : 3 -chosen so as to match closely the density and index of refraction of the particles. The density matching of the particles and the solvent is needed to avoid sedimentation at room temperature. The refractive index matching provides nearly transparent sample making it suitable for visualizing through microscope and at the same time minimizes inter particle van der Waals forces. The organic salt TBAB (tetra-butylammoniumbromide) is added to the suspension to further screen possible residual charges.

To prepare samples of different volume fractions, a suspension with a reference volume fraction is needed first. We start with a suspension of arbitrary volume fraction and centrifuge this to form a dense sediment followed by the removal of weighed amount of clear supernatant liquid. This results to a sample with a volume fraction close to random close packing, 0.64. Any sample with desired volume fractions is then obtained by adding weighted amount of solvent to this reference sample.

Finally, to verify the hard-sphere behavior of the above samples, we allow the system to crystallize by waiting weeks or months, and measure the crystallization density, a very sensitive measure for deviations from the hard-sphere behavior; it agrees to within a fraction of a percent to that of true hard spheres.
2.5 Confocal Microscopy

Optical microscopy also referred to as the “light microscopy” uses visible light and a system of lenses to magnify images of smaller objects which will be otherwise invisible by the naked eye. Microscopy started with the simple experiments of two Dutch spectacle makers, Zaccharias Janssen and his father Hans in the year about 1590 the modern optical microscope has evolved through the contributions of various scientists like Galileo Galilei, Anton Van Leeuwenhoek and Robert Hooke in sixteenth century. Today it has become a powerful visualization tool in the domain of micron and submicron length scales for a wide variety of disciplines like biology, nanophysics and micro-electronics. Nevertheless, visualizing deep inside a sample like biological tissues or dense colloidal suspensions remain difficult by a conventional optical microscope due to multiple scattering events leading to blurred images. These issues were first addressed by Marvin Minksky in 1950s which provides the basic foundation of confocal microscopy as elaborated in the section below.

2.5.1 Laser Scanning Microscopy

In 1961, Marvin Minksky has proposed a two fold solution - point by point illumination of the sample to minimize aberrant rays of scattered light as well as introduction of a pinhole aperture in the image plane eliminating all those rays emitted other than the focal plane, thus creating a better quality image than wide field imaging where the whole object is illuminated at the same time.

The light rays emerging from the pinhole is finally measured by a detector such as a photomultiplier tube. Figure 2.8 shows schematic of a confocal microscope. Now, constructing the image of the whole specimen in 2D or 3D requires scanning over a regular raster in the specimen. While the first confocal microscopes used a translating stage, modern day Confocal microscopes use lasers as a light source and scan across the sample to visualize each point inside it- this is called Laser Scanning Confocal Microscopy (LSCM) [22, 23, 24]. In present study we use a LSCM (Carl Zeiss, LSM5, live) with a high speed line scanning technique as shown in Fig. 2.9 to obtain the images of the fluorescent colloidal samples under study. Use of fluorescent particles further gives higher contrast as a filter blocks everything except the fluorescent wavelength.
2.6 Resolution

The resolution of any optical system is the ability to clearly determine two separate points, or objects, as singular, distinguished entities. In a
confocal microscope, the image of a point-like source is a three dimensional pattern known as ‘point spread function’ (psf) [23, 25] due to the diffraction through the circular aperture (pinhole). The transverse cross-section of the psf on the image plane is an Airy disc, whose size depends on the numerical aperture of the objective lens as well as on the wavelength of the light source. Generally, two closely spaced luminous points in the sample plane results into overlapping discs leading to an intensity distribution with two peaks as shown in Fig. 2.10. Now a minimum separation is required between the discs to create a reasonable ‘dip’ in between, for the peaks to be resolved -this sets the maximum resolution of the microscope. Following Rayleigh criteria this separation is the full width half maximum, FWHM of the airy disc (when the first minimum of an airy disc aligns with the central maximum of the second one) leading to a dip of roughly about 26%. For the optical setup of most commercially available confocal microscopes this separation is about 200 nm.

It is important to note that the precision of determining the position
of a light source is different from the resolution discussed above. The position of an isolated fluorescent point-like source corresponds to the ‘center of mass’ of its spatially extended airy disc image. If the disc is about \( N \) pixel wide and each pixel is \( M \) micrometers across, the center of the disc can be estimated to \( \approx M/N \) accuracy, which is higher than the optical resolution. In the present study this uncertainty in detecting the position of a single particle is \( \approx 28 \text{nm} \). This has been found from the standard deviation of the distribution positions of a set of particles glued on a slide and is discussed in more detail in chapter 3.

### 2.7 Scanning

The term scanning implies sequential illumination or observations of a selected section of an objective. The portion of the sample to be imaged by the microscope has to be scanned by the available light source. In the initial period stage scanners were used where the sample was translated while the optical system remained fixed. Gradually this has been improved by the introduction of galvanometers which move the mirror back and forth in a sawtooth pattern to scan the sample plane. The speed of most confocal microscopes is limited by the rate at which the mirrors can scan the entire sample plane. However, use of galvanometers is still a slow process even for a moderately sized sample. For example, a \( 512 \times 512 \) pixel image taken at video rates (30 frames s\(^{-1}\)) requires the galvanometer to scan a single direction at a frequency of \( \approx 30 \times 512 = 15 \text{kHz} \), much faster than its operating specifications of a few kilohertz. In recent times two designs are used to overcome this limitation and capture images at high speeds: (1) acousto-optic deflectors (AODs) and (2) Nipkow discs.

The present confocal set up uses the AOD technique for scanning, the maximum possible frame rate can be achieved is 120 frames per sec for an image size of \( 512 \times 512 \) pixels. The set of measurements presented here have been done mostly at a frame rate of about 20 – 30 frames/sec with the image size same as above. Scanning at higher frame rates causes bleaching of the colloidal particles leading to images reduced contrast.
2.8 Data Acquisition

We image the colloidal particles in the sample cell using an oil immersion objective that has a magnification of 63x and a numerical aperture of 1.4. The Zeiss LSM 5 microscope uses a line scanner that sequentially illuminates a selected section of the sample to be imaged, and its speed is limited by the rate at which entire sample plane is scanned. Particle positions have been recorded over a two dimensional plane inside the sample cell. The depth of this focal plane, $Z$, is controlled by a piezo-element mounted on the objective of microscope. We fix the position of the objective such that it’s focal plane is, at least, 20 – 25$\mu$m away from boundaries and acquire a time series of images. We then use particle tracking software IDL to detect the particle positions in each frame. Figure 2.11 shows an image frame of a dense colloidal glass with particle centers identified using the above software.

![Image of colloidal particles](image_url)
Bibliography


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